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Direct Acid Leaching of Vanadium from Stone Coal

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Abstract: This paper focused on optimizing the process conditions of direct acid leaching process to enhance the leaching efficiency of leaching vanadium from the stone coal. Orthogonal experiments and single factor experiments were conducted to investigate the effect of the influential factors of direct acid leaching on vanadium leaching ratio. The results showed that the vanadium leaching ratio reached the maximum value of 89.22 % under the optimal process conditions of CaF_2 dosage 5 mass%, H_2SO_4 dosage 40 mass%, leaching temperature 95 °C and leaching time 10 h. Furthermore, the reaction mechanisms of the main influencing factors were analyzed. Finally, the two-stage counter-current leaching process was adopted to decrease the consumption of sulfuric acid and neutralizer, and the results indicated that the consumption of sulfuric acid decreased 12.50 % as well as neutralizer decreased 35.80 %.

Keywords: vanadium, stone coal, direct acid leaching, counter-current leaching

Introduction

Vanadium is an important strategic material that is widely used in steel manufacture, aerospace, chemical industry and textile fields due to its superior properties such as tensile strength, hardness and fatigue resistance [1–3]. In China, stone coal is one of the primary mineral resources containing vanadium, in which the total reserve of vanadium accounts for more than 87 % of the domestic reserve of vanadium [4–6]. Therefore, more and more attention has been paid to research on extracting vanadium from stone coal.

Generally, most vanadium in stone coal exists in terms of isomorphism where V^{3+} substitutes for Al^{3+} in the crystal lattice of aluminosilicates including muscovite, tourmaline and garnet, because V^{3+} has similar electronegativity and ionic radius to Al^{3+} [7, 8]. In addition, small amounts of vanadium in the form of adsorbed state adsorb on the surface of clay minerals such as kaolin and dickite. For extracting vanadium from stone coal, it is necessary to break down the crystal structure of vanadium-bearing minerals. The traditional technology includes chloridizing roasting and water leaching processes, whereas the low vanadium recovery and the serious environment pollution make this technique limited [9, 10]. For the past few years, a large amount of researchers has been devoted to researching the novel technology of recovering vanadium from stone coal, such as blank roasting-acid leaching technique, blank roasting-alkali leaching technique, calcified roasting-carbonate leaching technique and direct acid leaching technique. Among these lately developed techniques, direct acid leaching attracts increasing attention due to the stringent legislation concerning environmental protection. As the roasting process is omitted, the direct acid leaching technique could lower the energy consumption and reduce the discharge of exhaust gasses. However, in some cases, the low leaching efficiency limits the application of this technique.

In this paper, the effects of sulfuric acid dosage, calcium fluoride dosage, leaching time and leaching temperature on vanadium leaching ratio were studied by orthogonal experiments to determine the main influential factors of direct acid leaching process. Furthermore, the single-factor experiments were conducted to investigate the effects of main influential factors on vanadium leaching ratio. As a result, the optimal process conditions of direct acid leaching were obtained and the reaction mechanisms of main influential factors were discussed. Finally, the intensification of leaching with H_2SO_4 was investigated along with the two-stage counter-current leaching process.

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Experimental

Materials

The raw stone coal used in this study was taken from Henan province in China. The dried ore was ground and sieved to the particle size less than 0.25 mm accounting for 95 % in this study. The obtained ore was referred to as raw ore throughout this work. The chemical compositions of the raw ore analyzed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) and X-Ray Fluorescence (XRF) were shown in Table 1, which revealed that the amount of V_2O_5 was 0.82 %. The crystal structure of the raw ore analyzed by X-Ray Diffraction (XRD) was shown in Figure 3(a), indicating that the main minerals were quartz, muscovite and dickite. Combing the results of electron microprobe (EPMA), ICP, XRF and XRD, the mass proportion of the main minerals in the raw ore were shown in Table 2 and the mineral compositions of the main vanadium-bearing minerals were shown in Table 3. On the basis of above analysis, it could be concluded that 75.09 % vanadium distributed in muscovite and 22.16 % vanadium distributed in dickite. In addition, 2.46 % vanadium existed in other minerals. All the reagents including sulfuric acid and calcium fluoride used for leaching were of analytical grade. The dosage of chemical reagents involved was defined as the mass ratio of chemical reagent to the raw ore.

Methods

Leaching experiments were carried out in a magnetic stirrer containing a contact thermometer. A measured amount of calcium fluoride and a predetermined volume of sulfuric acid were charged to a flask and heated to a specific temperature while being magnetically stirred. Then, 100 g of raw ore was added to the flask and the reaction time was initiated. After the required time, the slurries were separated by vacuum filtration and the residues were washed with distilled water. Finally, the filter cake was dried overnight at 105 °C. Unless special instructions, the liquid to solid ratio was 1.2:1 in this work. The obtained residues were analyzed for chemical compositions by ICP-AES method. The vanadium leaching ratio was calculated by the following equation:

$$\theta = \frac{\alpha - \beta}{\alpha} \times 100\% \tag{1}$$

Where, θ is the vanadium leaching ratio (%), α is the vanadium quantity of raw ore (g), β is the vanadium quantity of leaching residue (g). The crystal structure of residues was analyzed by XRD method.

In order to reduce the consumption of chemical reagents and facilitate the follow-up solvent extraction process, two-stage counter-current leaching process was

Table 1: Main chemical compositions of the raw ore (mass%).

V_2O_5	SiO_2	Al_2O_3	CaO	MgO	K_2O	TFe	S	Ba	C
0.82	62.63	10.02	0.20	0.76	1.59	2.18	2.82	2.02	10.38

Table 2: The mass proportion of the main minerals in the raw ore (mass%).

Minerals	Quartz	Dickite	Stone Coal	Muscovite	Barite	Pyrite	Anorthose	Hematite	Others
Mass Proportion (%)	49.1	29.3	10.4	3.4	3.4	0.9	0.9	1.7	0.9

Table 3: Mineral compositions of main vanadium-bearing minerals through EPMA (mass%).

Minerals	V_2O_5	SiO_2	Al_2O_3	CaO	MgO	K_2O	FeO	SO_3	Cr_2O_3
Muscovite	18.11	45.09	18.16	0.16	3.00	6.04	0.51	2.46	0.74
Dickite	0.62	47.52	37.24	0.07	0.11	0.01	1.69	0.15	0.21

investigated. The experimental procedure was shown in Figure 1, where R was the raw ore, S was the sulfuric acid and L was the leaching solution. The leaching solution in 1st stage was adopted as the leaching agent for the 2nd stage with a small quantity of sulfuric acid.

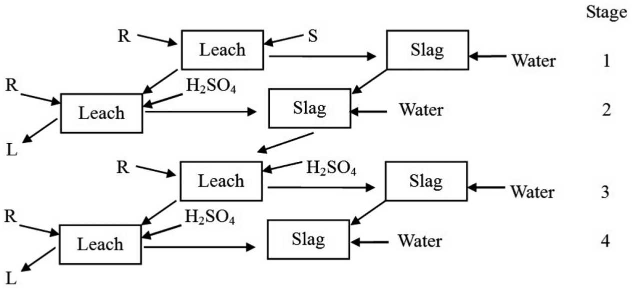

Figure 1: The flow chart of two-stage counter-current leaching.

Results and discussion

Orthogonal experimental results

The orthogonal experiments were made to investigate the effects of the influential factors on vanadium leaching ratio. The 4-factor and 4-level orthogonal array L_{16} (4^4) was employed. Meanwhile, the influential factors were leaching temperature (A), leaching time (B), sulfuric acid dosage (C) and calcium fluoride dosage (D). The experimental conditions of the orthogonal experiments were listed in Table 4 and the results were listed in Table 5.

Table 4: Experimental conditions of orthogonal experiments.

Experiments	A (°C)	B (h)	C (mass%)	D (mass%)
1	75	2	10	1
2	85	4	20	3
3	95	6	30	5
4	105	8	40	7

According to the results of orthogonal experiments, it can be seen that vanadium could be effectively leached in proper process conditions. When leaching temperature was 75 °C, leaching time was 8 h, CaF_2 dosage was 7 mass% and H_2SO_4 dosage was 35 mass%, the vanadium leaching ratio reached 79.32 %. Furthermore, the impact factors of the influential factors were R_A 2.67, R_B 4.04, R_C 33.07 and R_D 5.27. In conclusion, the effects on vanadium leaching ratio was $R_C > R_D > R_B > R_A$. It can be seen that sulfuric acid dosage may affect the leaching ratio significantly, whereas calcium fluoride dosage and leaching time slightly. The effect of leaching temperature was small. Moreover, vanadium leaching ratio was in direct proportion to sulfuric acid dosage, calcium fluoride dosage, leaching time and leaching temperature.

Table 5: Orthogonal experimental results of direct acid leaching.

Experiments	A (°C)	B (h)	C (mass %)	D (mass %)	Leaching ratio (%)
1	75	2	20	1	38.57
2	75	4	25	3	50.21
3	75	6	30	5	67.58
4	75	8	35	7	79.32
5	85	2	25	5	55.69
6	85	4	20	7	42.50
7	85	6	35	1	67.78
8	85	8	30	3	71.98
9	95	2	30	7	68.50
10	95	4	35	5	78.54
11	95	6	20	3	41.98
12	95	8	25	1	57.35
13	105	2	35	3	72.69
14	105	4	30	1	64.57
15	105	6	25	7	59.05
16	105	8	20	5	42.98
K_1	235.68	235.45	166.03	228.27	
K_2	237.95	235.82	222.3	236.86	
K_3	246.37	236.39	272.63	244.79	
K_4	239.29	251.63	298.33	249.37	
k_1	58.92	58.86	41.51	57.07	
k_2	59.49	58.96	55.58	59.22	
k_3	61.59	59.10	68.16	61.20	
k_4	59.82	62.91	74.58	62.34	
R	2.67	4.04	33.07	5.27	

Single-factor experimental results

In order to further improve the leaching efficiency of vanadium and optimize the process conditions of direct acid leaching process, the effects of sulfuric acid dosage, calcium fluoride dosage and leaching time on vanadium leaching ratio were investigated by single-factor experiments, and the reaction mechanisms of the influential factors were discussed.

Effect of sulfuric acid dosage

The effect of sulfuric acid dosage in the range of 30 mass%-50 mass% (mass ratio of H_2SO_4 to raw ore) was investigated under the following conditions: leaching time 12 h, CaF_2 dosage 5 mass% and leaching temperature 95 °C. The relationship between sulfuric acid dosage and vanadium leaching ratio was shown in Figure 2.

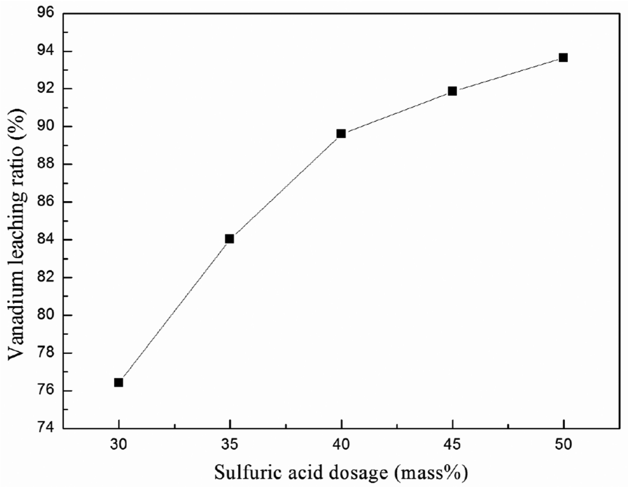

Figure 2: Effect of sulfuric acid dosage on vanadium leaching ratio.

It can be found that vanadium leaching ratio increased from 76.42 % to 89.61 % by increasing H_2SO_4 dosage from 30 mass% to 40 mass%. Nevertheless, the increase of vanadium leaching ratio became slowly with further increasing H_2SO_4 dosage, and a maximum value of 93.65 % was obtained at 50 mass% H_2SO_4 dosage.

The principle of direct acid leaching is that under high temperature and high acid concentration, H^+ could diffuse into the crystal lattice and substitute for Al^{3+}, resulting in the decomposition of the vanadium-bearing minerals [11, 12]. Then, V^{3+} is oxidized to VO^{2+} by oxygen from the air with vigorous stirring. Therefore, the higher concentration of sulfuric acid is benefit to the replacement of Al^{3+}, because H^+ had sufficient energy to damage the crystal structure of vanadium-bearing minerals. Considering the costing and the equipment, H_2SO_4 dosage of 40 mass% was optimal.

Figure 3 presented the XRD patterns of raw ore and leaching residues by H_2SO_4 leaching. As shown in Figure 3(a), the main minerals of raw ore was quartz and the main vanadium-bearing minerals were muscovite and dickite. As shown in Figure 3(b), the diffraction peak of muscovite and dickite completely disappeared, which confirmed that the crystal structure of the vanadium-bearing minerals was entirely destroyed, leaving the diffraction peaks of quartz and gypsum.

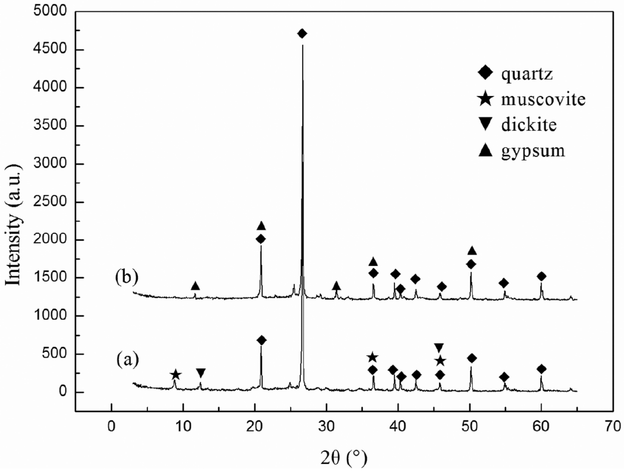

Figure 3: XRD patterns of (a) raw ore; (b) raw ore leached under following conditions: leaching time 12 h, CaF_2 dosage 5 wt. %, H_2SO_4 dosage 50 wt. % and leaching temperature 95℃.

Effect of calcium fluoride dosage

A variation from 1 mass% to 9 mass% (mass ratio of CaF_2 to raw ore) of the calcium fluoride dosage was expected to increase the leaching efficiency of vanadium. The effect of calcium fluoride dosage on vanadium leaching ratio was carried out under the following conditions: leaching time 12 h, H_2SO_4 dosage 40 mass% and leaching temperature 95 °C. The vanadium leaching ratio versus calcium fluoride dosage was shown in Figure 4.

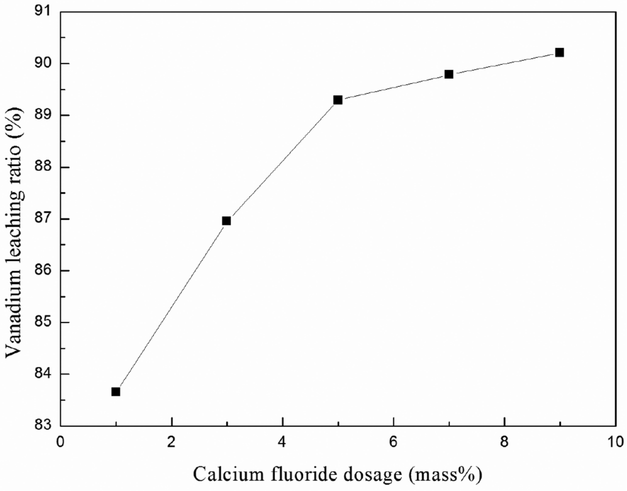

Figure 4: Effect of calcium fluoride dosage on vanadium leaching ratio.

It can be seen that vanadium leaching ratio increased from 83.65 % to 89.29 % with an increase in CaF_2 dosage from 1 mass% to 5 mass%, which indicated that the addition of CaF_2 contributes to an improved leaching recovery of vanadium. The mechanism is that CaF_2 react with sulfuric acid to generate weak electrolyte hydrofluoric acid and slightly soluble substance $CaSO_4$ in the acidic solution [13, 14]. Then, fluoride ions combine with silicium ions and aluminium ions to generate SiF_6^{2-} and AlF_5^{2-} because of its strong electronegativity [15]. As a result, the Si-O bond and Al-O bond in the aluminosilicate are fractured, and therefore the crystal structure of vanadium-bearing minerals is broken down. The possible chemical reaction equations could be presented as follows:

$$CaF_2 + 2H^+ + [SO_4]^{2-} \Leftrightarrow 2HF(aq) + CaSO_4 \downarrow \tag{2}$$

$$K(Al, V)_2[AlSi_3O_{10}](OH)_2 + 11HF + 3H^+ + O_2 \Leftrightarrow 2SiO_2 \downarrow + VO_2^{2+} + K^+ + Al^{3+} + [SiF_6]^{2-} + [AlF_5]^{2-} + 8H_2O \tag{3}$$

$$Al_4[Si_4O_{10}](OH)_8 + 11HF + 5H^+ \Leftrightarrow 3SiO_2 \downarrow + [SiF_6]^{2-} + [AlF_5]^{2-} + 3Al^{3+} + 12H_2O \tag{4}$$

With further increase of CaF_2 dosage, vanadium leaching ratio increased slowly and reached the maximum value of 90.21 % when CaF_2 dosage was 9 mass%.

Figure 5 presented the XRD patterns of leaching residues in different CaF_2 dosage. Figure 5(a) illustrated that though about 70 % vanadium was extracted by acid leaching without CaF_2, the characteristic peaks of muscovite and dickite were clearly observed in the low angle of the XRD images. As shown in Figure 5(b), the diffraction peak of dickite disappeared, whereas the diffraction peak of muscovite still existed. This phenomenon is attributed to the fact that vanadium in muscovite is embedded in the crystal lattice by taking place of aluminum as isomorphism state, which is more difficult to be leached than that existing in dickite as adsorbed state. Meanwhile, new phase of gypsum generated according to equation (2). For the sample leached with 10 mass% CaF_2 dosage shown in Figure 5(c), the characteristic peaks of muscovite completely disappeared, which indicated that CaF_2 favored the decomposition of aluminosilicate minerals. In addition, the generated quartz and gypsum intensified the intensity of quartz peak and gypsum peak.

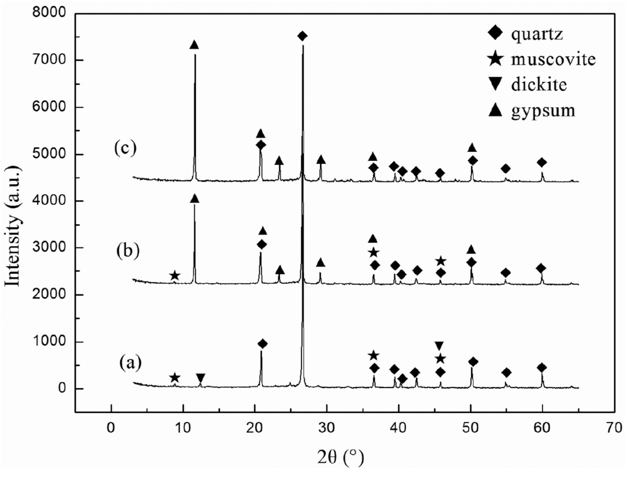

Figure 5: XRD patterns of stone coal leached under following conditions: leaching time 12 h, H_2SO_4 dosage 40 wt. % and leaching temperature 95°C: (a) residue without CaF_2; (b) residue with 5 wt. % CaF_2; (c) residue with 10 wt. % CaF_2.

Effect of leaching time

The effect of leaching time in the range of 6 to 14 h was investigated under the following conditions: H_2SO_4 dosage 40 mass%, CaF_2 dosage 5 mass% and leaching temperature 95 °C. The relationship between leaching time and vanadium leaching ratio was shown in Figure 6.

Figure 6 illustrated that the vanadium leaching ratio increased significantly in the range from 6 to 10 h, and 89.07 % of vanadium was leached at 10 h. The reason was that with the increase of leaching time, the vanadium-bearing minerals could sufficiently react with sulfuric acid and calcium fluoride, hence more vanadium was released in the leaching solution [16]. However, an increase in leaching time from 10 to 14 h had no remarkable variation in extracting vanadium. Therefore, the leaching time of 10 h was optimal.

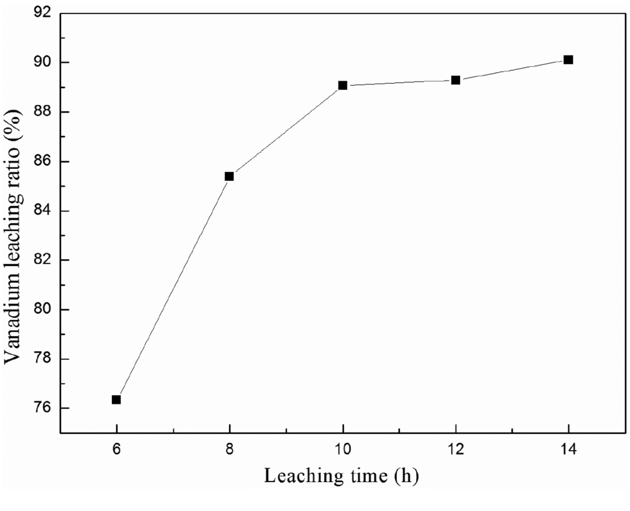

Figure 6: Effect of leaching time on vanadium leaching ratio.

According to above results, the optimal process conditions of direct acid leaching for vanadium were CaF_2 dosage 5 mass%, H_2SO_4 dosage 40 mass%, leaching temperature 95 °C and leaching time 10 h. The reproducibility tests were carried out under these optimal conditions, and the results were listed in Table 6. It can be observed that the vanadium leaching ratio under the optimal process conditions had good reproducibility, and the average value was 89.22 %.

Table 6: Results of reproducible tests under the optimal process conditions.

Experiments	1	2	3	4
Leaching ratio (%)	89.19	89.25	89.37	89.06

Effect of counter-current leaching

The high sulfuric acid concentration was employed in direct acid leaching process to obtain high vanadium recovery, whereas these caused high-cost consumptions of sulfuric acid. Furthermore, the residual sulfuric acid in leaching solution also need vast neutralizer to adjust the pH to a certain value of 2.3–2.4 which was the requirement for the follow-up solvent extraction process. Therefore, the two-stage counter-current leaching process was put forward to lower the consumption of sulfuric acid and neutralizer.

The effect of H_2SO_4 dosage on vanadium leaching ratio for two-stage counter-current leaching process was studied under the following conditions: CaF_2 dosage 5 mass%, leaching temperature 95 °C and leaching time 10 h. According to the results of experiments illustrated in Table 7, vanadium leaching ratio decreased with decreasing average H_2SO_4 dosage. For reducing the consumption of sulfuric acid, average H_2SO_4 dosage of 35 mass% (H_2SO_4 dosage in 1st stage was 40 mass% and H_2SO_4 dosage in 2nd stage was 30 mass%) was adopted for further experiments. The corresponding vanadium leaching ratio was 86.48 %, which was slightly decreased compared to direct acid leaching process.

Table 7: Effect of H_2SO_4 dosage on vanadium leaching ratio for two-stage counter-current leaching.

Experiments	H_2SO_4 dosage (mass%)		Average H_2SO_4 dosage (mass%)	Average leaching ratio (%)
	1st stage	2nd stage		
1	40	30	35.00	86.48
2	40	35	37.50	88.25
3	45	35	40.00	90.18
4	45	25	35.00	86.37

To adjust the pH value of 2.3–2.4 for the subsequent extraction process, ammonium bicarbonate was chosen as the neutralizer to neutralize the leaching solution. The effect of leaching methods on neutralizer dosage was shown in Table 8. It can be seen that for direct acid leaching, the neutralizer dosage (mass ratio of neutralizer to raw ore) was about 14 mass% at H_2SO_4 dosage 40 mass%, whereas the neutralizer dosage in counter-current leaching process was about 9 mass% at H_2SO_4 dosage 35 mass%. The results showed that the consumption of sulfuric acid decreased 12.50 % as well as neutralizer decreased 35.80 %, which demonstrated that the counter-current leaching could evidently decline the consumption of sulfuric acid and neutralizer.

Table 8: Effect of leaching methods on neutralizer dosage.

Experiments	H_2SO_4 dosage (mass%)	Leaching methods	Neutralizer dosage (mass%)
1	40	Direct leaching	14.22
2	40	Direct leaching	14.07
3	35	Counter-current leaching	9.15
4	35	Counter-current leaching	9.10
5	35	Counter-current leaching	9.00

In addition, the vanadium concentration in leaching solution of counter-current leaching process was 6.48 g/L while in direct acid leaching process was 4.59 g/L, which indicated that the vanadium concentration in leaching solution increased more than 41 % by using counter-current leaching process. The reason was that the leaching solution had been leached twice by the raw ore in 1st stage and 2nd stage. As a consequence, it is obvious that the increase of vanadium concentration largely reduced the amount of leaching solution which needed to be treated for the follow-up solvent extraction process, hence the production efficiency for the industrial production could be apparently enhanced.

In conclusion, although vanadium leaching ratio was slightly decreased, the two-stage counter-current leaching process could not only reduce the consumption of sulfuric acid and neutralizer, but also increase the vanadium concentration in leaching solution. Therefore, it is reasonable to use counter-current leaching process to produce vanadium in industrial production.

Conclusions

From the results of this study, the following conclusions could be drawn:

(1) The results of orthogonal experiments indicated that vanadium leaching ratio increased with increasing sulfuric acid dosage, calcium fluoride dosage, leaching time and leaching temperature. Moreover, sulfuric acid dosage significantly affected vanadium leaching ratio, whereas calcium fluoride dosage and leaching time slightly. The effect of leaching temperature was small.

(2) The results of single factor experiments indicated that the vanadium leaching ratio reached the maximum value of 89.22 % under the optimal conditions: CaF_2 dosage 5 mass%, H_2SO_4 dosage 40 mass%, leaching temperature 95 °C and leaching time 10 h. XRD results showed that the crystal structure of the vanadium-bearing minerals was completely destroyed.

(3) By using the two-stage counter-current leaching process, the consumption of sulfuric acid decreased 12.50 % as well as neutralizer decreased 35.80 % compared to the direct acid leaching process. In addition, the vanadium concentration in leaching solution increased more than 41 % in the two-stage counter-current leaching process, which evidently facilitated the follow-up solvent extraction process.

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